(12) UK Patent Application (19) GB (11) 2 138 796 A

(43) Application published 31 Oct 1984

(21) Application No 8311059

(22) Date of filing 22 Apr 1983

(51) INT CL[3]
C23F 11/18

(52) Domestic classification
C1C 253 254 315 324 463 B
U1S 1349 1471 1976 1978 3010 3013 C1C

(56) Documents cited
None

(58) Field of search
C1C

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(54) Preventing corrosion

(57) In a process for improving the initial activity of activated hydrazine employed for the prevention of corrosion in boiler feed water and for the wet preservation of idle plant, the initial activity of hydrazine solutions activated with complexes of trivalent cobalt are increased in relation to oxygen dissolved in water by adding trivalent phenols, preferably pyrogallol, in small quantitites to the hydrazine solution containing activator.

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SPECIFICATION

Process for improving the initial activity of activated hydrazine

This invention relates to a process for improving the initial activity of hydrazine in relation to oxygen dissolved in water, the hydrazine being activated by the addition of complexes of trivalent cobalt with inorganic ligands as complex-formers. Activated hydrazine is used as a means for the removal of oxygen from water, particularly from boiler feed water and from water employed for the preservation of idle plant in order to prevent corrosion of tanks, pipes, heat exchangers and other parts.

For the removal of oxygen dissolved in water various processes are employed. Preference is given to the use of hydrazine which even at low temperatures and with the addition of suitable activators reacts with oxygen dissolved in water to form harmless hydrogen. Cationic and anionic complexes of trivalent cobalt, with inorganic ligands as complex-formers, have been proposed as particularly suitable activators, (GB/83 Ref: 39291). However hydrazine activated in this way does not immediately reach full reaction speed in relation to oxygen dissolved in water.

It has been suggested that these drawbacks may be overcome by gasification, using air, of the hydrazine solution containing activator. This system suffers from the drawback that a special step has to be introduced into the process in order to ensure satisfactory initial activity. A further disadvantage is that with the use of hydrazine solutions in the customary commercial concentrations exhausted air contains hydrazine vapour and must not be directly discharged into the environment.

This invention seeks to enable the initial activity of activated hydrazine in relation to oxygen dissolved in water to be improved when the activators used consist of complexes of the trivalent cobalt with inorganic ligands serving as complex-formers.

For this a suitable activator system is required which would ensure that hydrazine solution provided with the activators in moderate concentration would immediately reach a high reaction speed in relation to oxygen dissolved in water, the process not requiring gasification with air.

According to this invention there is provided a process for improving the initial activity of hydrazine in relation to aquous dissolved oxygen, the hydrazine having been activated by the addition of complexes of the trivalent cobalt with inorganic liguands as complex-formers, wherein trivalent phenols are added as coactivators to the hydrazine solution. These compounds are not sufficiently effective as sole additives for hydrazine and surprisingly do not have an effect until used in conjunction with complexes of trivalent cobalt. A particularly suitable agent is pyrogallol, but oxyhydroquinone and phloroglucin are likewise effective. One advantage of the process is that a high reaction speed is already obtained with only slight quantities. Additions of the aforementioned coactivators amounting to 0.05 to 0.5% by mass, in relation to the ordinary commercial hydrazine solution of 15 to 25% strength, or 5 to 50% in relation to the cobalt complex activator content, are sufficient. Higher concentrations are possible but do not offer any special advantages. The small quantities of organic coactivators added enable the disadvantages otherwise observable with organic additives to be avoided. It is a particularly advantage that the effect does not decrease as time proceeds during removal of oxygen. The coactivators are dissolved, prior to use, in the hydrazine solution containing activator.

Examples

Example 1

In an aqueous hydrazine solution which contains 220 g of hydrazine per litre and which has been activated with 0.1% by mass of pentamminocobalt (III)-trichloride or sodium hexanitritocobaltate (III), 0.1 g of oxyhydroquinone per litre was dissolved. 1 ml of the solution containing coactivator was mixed into one litre of an oxygenous water containing 6 to 7 mg $O_2/1$ in a dissolved state. The oxygenous water had been set in advance to a pH value of 9.3 or 10.5. The temperature amounted to 293°K. After a reaction time of 10 minutes the residual oxygen content was measured. The water was then gasified by passing air through it for 10 minutes and thus once again supplied with oxygen.

This process was repeated. The oxygen content was in each case determined immediately after the gasification and after a reaction time of 10 minutes.

The results are shown in Tables 1 to 4.

Table 1

Catalyst: 1 g of pentamminocobalt-(III)-chloride and 0.1g of pyrogallol per litre of hydrazine solution

Gasification	pH value	Residual Start	oxygen in mg/1 After 10 minute reaction time
Without	10.5	5.8	0.7
1	10.5	2.7	0.6
2	10.5	1.7	Traces
3	10.5	0.8	0
4	10.5	1.2	0
5	10.5	0.8	0
6	10.5	0.7	0
Without	9.3	5.8	1.2
1	9.3	3.5	0.4
2	9.3	2.1	Traces
3	9.3	0.8	Traces
4	9.3	0.8	0
5	9.3	1.5	0
6	9.3	1.4	0

Table 2

Catalyst: 1 g of sodiumhexanitritocabalt-(III) and 0.1 g of pyrogallol per litre of hydrazine solution

Gasification	pH value	Residual Start	oxygen in mg/1 After 10 minute reaction time
Without	10.5	6.0	0.7
1	10.5	0.2	0
2	10.5	0	0
3	10.5	0	0
4	10.5	0	0
5	10.5	0	0
6	10.5	0	0
Without	9.5	5.7	0.5
1	9.5	0.1	0
2	9.5	0.8	0
3	9.5	0.1	0
4	9.5	0	0
5	9.5	0	0
6	9.5	0	0

Table 3
Catalyst: 1 g of pentamminocobalt-(III)-chloride and 0.1 g of oxyhydroquinone per litre of hydrazine solution

Gasification	pH value	Residual Start	oxygen in mg/1 After 10 minute reaction time
Without	10.5	5.9	0.1
1	10.5	1.8	Traces
2	10.5	0.8	0
3	10.5	0.3	0
4	10.5	0.1	0
5	10.5	0.1	0
6	10.5	0.1	0
Without	9.5	5.8	0.5
1	9.5	2.3	0.1
2	9.5	2.0	0.1
3	9.5	0.2	Traces
4	9.5	0.4	0
5	9.5	0.4	0
6	9.5	0.6	0

Table 4
Catalyst: 1 g of sodiumhexanitritocobaltate-(III) and 0.1 g of oxyhydroquninone per litre of hydrazine solution

Gasification	pH value	Residual Start	oxygen in mg/1 After 10 minute reaction time
Without	10.5	6.1	0.05
1	10.5	0.4	Traces
2	10.5	0	0
3	10.5	0	0
4	10.5	0	0
5	10.5	0	0
6	10.5	0	0
Without	9.5	5.9	2.0
1	9.5	3.5	1.8
2	9.5	3.0	0.4
3	9.5	0.6	Traces
4	9.5	0.3	Traces
5	9.5	1.1	Traces
6	9.5	1.1	Traces

Example 2

An aqueous hydrazine solution containing 220 g of hydrazine per litre and free of cobalt complex activators was given an addition of 0.1 and 0.5 g of pyrogallol and phloroglucin or hydroxyquinone per litre. 1 ml of the hydrazine solution thus treated was mixed as in Example 1 (after a reaction time of 10 minutes) into one litre of oxygenous water and the residual oxygen content then measured. The temperature amounted to 293°K.

The pH value of the water was set to 10.5. The water was the gasified by passing air through it for 10 minutes and thus once again supplied with oxygen. This process was repeated a number of times. The oxygen content was in each case determined immediately following the gasification and after a reaction time of 10 minutes. The results are shown in Table 5.

Table 5
Organic compounds alone, with gasification repeated a number of times:

Concentration: 0.5 g per litre of hydrazine solution,
Temperature 293°K

Organic compound	pH value	Gasification	Residual Start	oxygen in mg/1 After 10 minute reaction time
Pyrogallol	10.5	Without	4.8	3.3
Pyrogallol	10.5	1	4.3	2.6
Pyrogallol	10.5	2	3.6	2.8
Pyrogallol	10.5	3	3.5	2.9
Pyrogallol	10.5	4	3.5	2.9
Pyrogallol	10.5	5	3.5	3.3
Pyrogallol	10.5	6	3.5	3.1
Phloroglucin	10.5	Without	4.3	3.7
Phloroglucin	10.5	1	4.4	4.0
Phloroglucin	10.5	2	4.3	3.7
Phloroglucin	10.5	3	4.2	3.7
Phloroglucin	10.5	4	3.7	3.7
Phloroglucin	10.5	5	3.7	3.7
Phloroglucin	10.5	6	4.0	3.9
Oxyhydroquinone	10.5	Without	4.3	0.3
Oxyhydroquinone	10.5	1	4.3	2.0
Oxyhydroquinone	10.5	2	2.8	1.7
Oxyhydroquinone	10.5	3	3.2	2.4
Oxyhydroquinone	10.5	4	3.3	2.6
Oxyhydroquinone	10.5	5	3.4	2.3
Oxyhydroquinone	10.5	6	3.3	2.5

CLAIMS

1. Process for improving the initial activity of hydrazine in relation to aquous dissolved oxygen, the hydrazine having been activated by the addition of complexes of trivalent cobalt with inorganic ligands as complex-formers, wherein trivalent phenols are added as coactivators to the hydrazine solution.
2. Process in accordance with Claim 1, wherein the coactivator used is pyrogallol.
3. Process in accordance with Claim 1 or 2, wherein the coactivators are used in quantities of 5 to 50% (by mass) in relation to the cobalt complex activator.
4. Process in accordance with Claim 3, wherein the quantity of coactivator used in 10%.
5. Process substantially as described herein and exemplified.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1984, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.